Structure of Manganese Zinc Ferrite Nanomagnets

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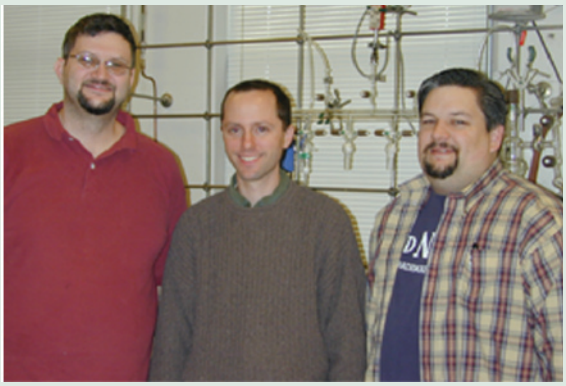
Scientists at the Naval Research Laboratory have synthesized nanoscale manganese zinc ferrite (MZFO) particles using colloidal aggregates of amphiphilic molecules (having a water-soluble and a water-insoluble component). By using a technique called extended x-ray absorption fine structure (EXAFS) spectroscopy at beamline X11A, the scientists have determined the distribution of the manganese, zinc, and iron ions between the lattice sites of MZFO to a precision of eight percentage points.

Nanoscale magnets hold great promise for a wide range of future technologies: Aside from improving the performance of microwave filters and power supplies, they could be used in targeted delivery of pharmaceuticals and as biological sensors. Although scientists have been synthesizing nanoscale magnets for many years, the magnetic particles have generally been produced with a wide range of sizes, whereas most applications require particles with a narrow size distribution, called monodisperse particles.



Authors (from left): Everett Carpenter, Scott Calvin, and Shannon Morrison

We created monodisperse nanoparticles made of manganese zinc ferrite (MZFO) by using micelles (**Figure 1**), which are colloidal aggregates of thousands of amphiphilic molecules (having a water-soluble and a water-insoluble component). The micelles were formed by adding a small amount of the surfactants nonylphenol poly(oxyethylene)$_5$ and nonylphenol poly(oxyethylene)$_9$ and water to cyclohexane. Micelle self-assembly sequesters the water into tiny droplets of a uniform size determined by the water-to-surfactant ratio, which limits the size of particles formed via aqueous reactions. In our case, the particles were approximately 11 nanometers in diameter.

In addition to the problem of monodispersion, the atomic-level structure of nanomagnets in their early development is not well known, so that the characteristics of devices made of nanomagnets are not well defined either. In the case of MZFOs, the manganese, zinc, and iron ions can each potentially reside in two different environments: tetrahedral sites surrounded by four oxygens, or octahedral sites surrounded by six oxygens. By knowing the distribution of the ions between these sites, scientists and engineers can better predict the performance of the materials made of MZFOs.

We studied the structure of MZFO by using extended x-ray absorption fine structure (EXAFS) spectroscopy at beamline X11A. In order to determine the distributions of the manganese, zinc, and iron ions, we first measured the ratio of absorbed photons versus the total incident photons. Then, we compared the experimental spectra to theoretical spectra, and developed a model of mixed ferrite materials for the purpose of extracting information from the absorption spectra.

Previous EXAFS studies of magnetic nanoparticles have looked at each metal absorption spectrum separately, allowing scientists to identify, for example, that the zinc ions were in a tetrahedral environment and that

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the iron and manganese were distributed between tetrahedral and octahedral environments. But, in these studies, scientists could not easily untangle the tetrahedral and octahedral contributions, and determine precise quantitative distributions.

In this study, we fit the models to all three metal edges simultaneously, so that the result was constrained to agree with the stoichiometry of the material and lead to a precision of about eight percentage points for the distribution of manganese, zinc, and iron ions. The technique outlined here promises to be an important tool in determining the structure of magnetic nanoparticle materials.

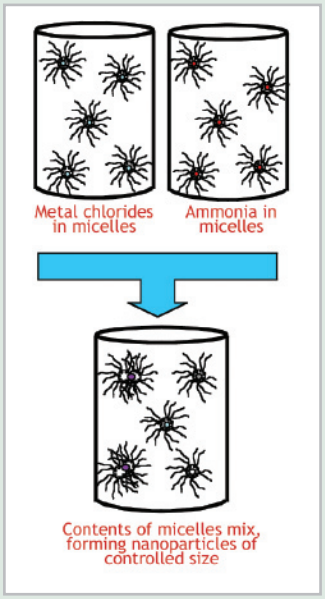

Figure 1. Schematic of reverse micellar method of nanoparticle synthesis.

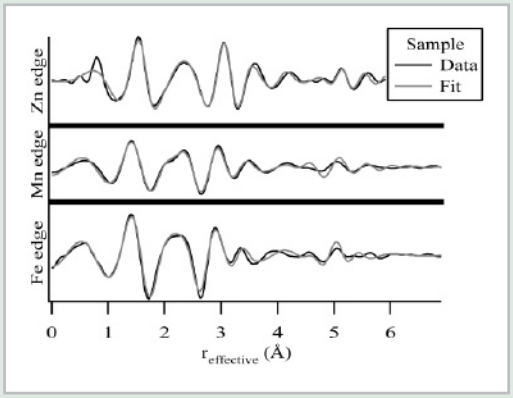

Figure 2. Real part of the Fourier transform of the EXAFS data for one sample, along with the fitted theoretical model. Above 1 Å the lower limit of validity for the fitting algorithm) the fitted models reproduce the data with high accuracy, confirming that the nanoparticles adopted the spinel ferrite structure.